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(71) Applicant *(for AU BB CA GB IE LK MN MW NZ SD only)*: UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4 4BQ (GB).

(71) Applicant *(for all designated States except AU BB CA GB IE LK MN MW NZ SD)*: UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(72) Inventors: VAN DALEN, Josef, Petrus; Kon. Wilhelminalaan 308a, NL-2274 AV Voorburg (NL). VAN PUTTE, Karel, P., A., M.; de Barch 2, NL-3155 BB Maasland (NL). VAN SLOOTEN, Ronald, Frederik; Charlotte Kohlerpad 29, NL-2331 KH Leiden (NL).

(74) Agent: SIKKEN, Antonius, H., J., M.; Unilever N.V., Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL).

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(54) Title: PROCESS FOR THE REFINING OF EDIBLE OILS

(57) Abstract

A method for refining triglyceride oils, preferably of natural origin. The method is particularly suitable for the refining of oils meant for direct consumption such as are sunflower oil, palm oil and olive oil. The method consists of a two-step treatment comprising a heating treatment and a subsequent stripping treatment. The stripping temperature is at 30-200 °C and the heating treatment consists of keeping the oil at an elevated but moderate temperature (30-180 °C). A stable oil results, which may be characterized further either by a specific flavour profile which may be appraised as natural and attractive or by the absence of any flavour.

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PROCESS FOR THE REFINING OF EDIBLE OILS

The present invention is concerned with a method for refining edible oils with the aim to avoid any refining step which is not considered natural.

Background of the invention

The purification process of a crude edible oil usually comprises the removal of phospholipids (degumming) by means of water, acid and/or a sorbent. Oils for which degumming was the first refining step still contain substances which have a negative influence on taste, smell and keepability. Those substances comprise inter alia free fatty acids and destabilising peroxydes. For the removal of several unwanted substances a process is used called deodorisation, which can be performed by stripping the oil with a stripping medium e.g. steam, at temperatures above 200°C. Stripping at such relatively high temperatures has the disadvantages that the oil may decompose and that unwanted and sometimes even toxic compounds are formed.

It has been realised that oils having a flavour which is much alike the natural flavour might be much appreciated by oil consumers. However, the natural flavour of an oil may suffer from the presence of substances which contribute to an off-flavour perception. The problem is to remove the

flavour deteriorating substances while preserving and preferably increasing the flavour improving substances, without being hindered by the disadvantages of the processes according to the state of the art.

The invention

The object of the invention is to provide a mild and cheap refining method for the purification of edible oils and in the same time to provide oils with a specific flavour profile or even without any flavour (bland flavour).

Surprisingly a refining process has been found comprising individual steps which are each considered as being natural, which in spite of the mild conditions applied, can afford a purified oil which is suited for direct consumption and which can be qualified as "natural". Its appearance and flavour are of a surprisingly high quality.

According to the invention a method is provided for refining a triglyceride oil which comprises acidifying the oil and removing substances which separate from the oil, followed by gas stripping of the oil at a temperature of 30-200°C, characterised in that the stripping treatment is preceded by a heat treatment, which consists of keeping the oil at a temperature of 30-180°C.
With this method the flavour profile of the oil can be modified, including the complete removal of flavour.

Detailed description

Without wanted to be limited by theory it is believed that during the heating treatment decomposition occurs of unwanted oil substances, particularly destabilising peroxides, into harmless or even flavour imparting com-

pounds such as ketones, aldehydes or alcohols.

The treatment of the invention is denoted as mild in contrast to the usual, demanding refining treatments comprising use of chemicals and/or high temperatures, such as alkaline deacidification, bleaching and deodorising at temperatures >200°C.

The temperature of the heat treatment preceding the stripping of the oil is in the range of 30-180°C, preferably 40-160°C and more preferably 60-160°C. A suitable duration of the heat treatment may be in the range of one hour to one week, and preferably is between 5-40 h. It goes without saying that when the process temperature is decreased, the process time should be increased to obtain sufficient effect. Therefore time and temperature should be properly attuned to each other so that a refined oil is obtained with a satisfying flavour.

On behalf of the removal of substances which separate from the oil an adsorbent, for example silica, may be admixed before filtration.

When the heat treatment according to the invention is carried out in the presence of an additive consisting of a relatively small amount of an acid and/or an antioxidant, preferably a tocopherol, the duration of the treatment may be considerably shortened.
For example, without the additive a suitable time is 14-15 h at a temperature of about 120°C, but with the additive the same effect is obtained within 7-8 h at the same temperature. The amount of additive is 10-2000 ppm, preferably 100-2000 ppm calculated on oil. A suitable amount is 500 ppm. On behalf of its addition the acid may be dissolved or dispersed in a suitable harmless liquid.

For acidifying the oil as mentioned above preferably

natural acids are used, which may advantageously be selected from the group comprising citric acid, tartaric acid, malic acid, lactic acid and acetic acid. Such natural acids are preferred as they contribute to the 'green' character of the refining method of the present invention. In this respect also natural extracts or compositions containing such acids are mentioned, like lemon-juice and the like.

The gas stripping is carried out according to methods known in the art with the proviso that preferably temperatures are practised which are moderate. Moderate stripping temperatures suitable for the purpose of this invention are defined as being in the range of 30-200°C. Preferably the temperature is in the range of 30-180°C and more preferably of 60-160°C. A suitable period of time for gas stripping is 1-100 h, preferably 1-10 h. By properly attuning stripping time and temperature it is possible to obtain an oil with a characteristic and attractive flavour profile or even an oil being completely disposed of flavour (bland flavour).

Although the process according to the invention can be used with any kind of edible oil, either from animal or vegetable origin, it is particularly suitable for the purification of natural oils which have been obtained from a natural source and which after a mild refining treatment are ready for direct consumption such as sunflower oil, palm oil, olive oil, rape seed oil etc.

The present refining treatment may be combined with other known mild treatments such as washing with water, centrifuging or filtration, comprising membrane filtration.

Stripping is suitably effected by blowing steam or an inert gas such as nitrogen through the oil.

During the heating period it is recommended to protect the

oil from the outer air by a nitrogen blanket to prevent oil oxydation.

Bland flavour oils which have been obtained by the process of the invention are characterised by a free fatty acids content of at least 0.1 wt.% and a POV-value of less than 1 or even less than 0.5.

Thus, according to the invention, it is possible to improve and to attune or to remove the flavour of an edible oil applying mild processing conditions and without the addition of non-natural flavour imparting substances to the oil.
The oil may be featured as a "natural" oil for still another reason because the process can dispose of the usual bleaching treatment which removes carotenoids, so that the natural colour of the oil is retained.

The oils according to the invention can be used as such for consumption, or they may be processed further. The invention therefore finally provides an edible composition containing a refined oil according to the invention. The refined oils according to the invention may be used for example as ingredients in the preparation of edible compositions, such as water and oil emulsions, e.g. mayonnaise, dressings, fat spreads or processed cheese. Since the fat component of such products may be quite substantial, consequentially the flavour of the oil may contribute considerably to the flavour of the end product.

The oil refined according to the invention still has most of the original carotenoids present, whereas an oil refined according to the art has no carotenoids left. The oil refined according to the invention can therefore be used as a natural colourant in products, e.g. spreads, having the advantage that no taste is present which could interfere

with the desired taste of the product.

The following Examples illustrate some specific embodiments of the present invention in greater detail. All percentages are % by weight on oil unless indicated otherwise.

Example 1

A 5 kg sample of a crude sunflower oil, containing phosphorous containing substances corresponding to 22 mg P/kg oil and free fatty acids corresponding to 0.69 %, was degummed at a temperature of 90°C. 0.10 % of a citric acid solution (50 % concentration) was added and after 15 min 0.2 % of water was added. After another 15 min 1.0 % of Trisyl (Davidson Chemical Division of W.R. Grace & Co.) was added and after 30 min water was removed from the mixture by drying at subatmospheric pressure until the water content was less than 0.1 %. After cooling the mixture to a temperature of 40°C, the solids were filtered off.

The degummed oil heated to 120°C oil was stirred for 15 h under N_2-blanketing and subsequently stripped with steam at 120°C for 5 h. The flavour was completely removed.
A reference sample (A) comprising the same oil, was subjected to the same degumming pretreatment, however, after filtration it was deodorised immediately by stripping with steam at 180°C for 5 h.
Another reference sample (B) comprising the same oil, was treated like sample (A) but stripped at 120°C for 5 h.

The analytical data of the crude oil, the oil refined by the method according to the invention and the reference sample (A) are listed in Table I.

The fresh taste of the oil prepared according to the example and the oil of sample (A) was good. Even after 28 weeks of storage the taste was still acceptable for both exemplified oils.

However, the oil sample (B) which had only been subjected to stripping at 120°C, was immediately rejected by a test panel.

Table I

Oil	FFA (% wt)	POV (meqO$_2$/kg)	P (mg-/kg)	Fe (mg-/kg)	E232 (1%/-1cm)	E268 (-1%/-1cm)
Crude	0.69	3.3	21.6	0.07	2.88	0.69
Inven-tion	0.55	0.3	<2	<0.01	2.77	1.11
Referen-ce (A)	0.03	0	<2	<0.01	2.57	1.33

Example 2

To a 5 kg sample of crude palm oil at a temperature of 90°C 0.10% of citric acid solution (50%) was added and after a residence time of 15 minutes 0.2% of water was added. After another 15 minutes 1.0% of Trisyl (Davidson Chemical Division of W.R. Grace & Co.) was added and 30 minutes later water was removed from the mixture by drying at subatmospheric pressure until the water content was less than 0.1%. After cooling the mixture to a temperature of 40°C, the solids were filtered off. The oil was then heated to 120°C, stirred for 15 hours under N_2 blanketing and subsequently deodorized for 5 hours at 120°C. The flavour of the oil was completely removed.

For comparison, a reference sample containing the same oil was subjected to traditional palm oil refining comprising alkaline neutralisation and bleaching according to the art and, after filtration, deodorizing at 240°C for 2 hours. The fresh taste of both treated oils was good.
The analytical data of the crude oil, the oil refined according to the invention and the reference are listed in Table II

Table II

	FFA (% wt)	POV (meqO_2/kg)	E232 (1%/1cm)	E268 (1%/-1cm)	Carotene (mg/kg)
Crude	4.40	4.3	1.82	0.45	497
Invention	3.97	0	1.43	0.35	377
Reference	0.08	0	2.10	1.19	0.4

Example 3

The same experiments as described in Example 1 were repeated on pilot plant scale (75 kg) with good result: in Table III the analytical data of the crude oil, the oil refined according to the invention and reference sample (A) are listed. After deodorization the fresh taste of the oil treated according to the invention and the reference sample A was excellent. After 6 months of storage at 15°C in plastic bottles the taste of both treated oils was still qualified as excellent.

Table III

	FFA	P	Fe	E_{232}	E_{268}	POV
Crude	0.69	13	0.14	2.39	0.24	4
Invention	0.65	<1	<0.01	2.54	0.61	0
Ref. A	0.03	<1	<0.01	n.m.	n.m.	0

Example 4

A crude sunflower oil was split in two equal samples. To one sample 0.1% citric acid (50% solution) was added, whereas to the second sample nothing was added. Subsequently both oils were heated under nitrogen for 10 hours at 120°C. In Table IV the POV values at different times are shown. This example clearly shows that the presence of citric acid during the heating treatment increases the decomposition rate of peroxides (indicated by decreasing POV-value).

Table IV

Time (hours)	POV ($meq.O_2/kg$)	
	Without citric acid	500 ppm citric acid
0	100	100
2	67	55
4	42	37
6	29	23
8	20	11
10	18	2

C L A I M S

1. Method for refining a triglyceride oil comprising acidifying the oil and removing substances which separate from the oil, followed by gas stripping of the oil at a temperature 30-200°C, characterised in that the stripping treatment is preceded by a heat treatment, consisting of keeping the oil at a temperature of 30-180°C, preferably 40-160°C.

2. Method according to claim 1, characterised in that during the heat treatment the oil is kept at a temperature of 60-160°C.

3. Method according to one or more of claims 1-2, characterised in that the duration of the heat treatment is comprised between one hour to one week, preferably between 5-40 h.

4. Method according to one or more of claims 1-3, characterised in that during the heat treatment the oil contains an additive consisting of an acid and/or an anti-oxidant, which amounts to 10-2000 ppm calculated on oil.

5. Method according to one or more of claims, 1-4 characterised in that for acidifying the oil a natural acid is used.

6. Method according claim 5, characterised in that the natural acid is selected from the group comprising citric acid, tartaric acid, malic acid, lactic acid and acetic acid or natural extracts or compositions containing such acids.

7. Method according to one or more of the preceding

claims, characterised in that, the gas stripping temperature is 30-180°C, preferably 60-160°C.

8. Method according to one or more of the preceding claims, characterised in that, the duration of the gas stripping is comprised between 1-100 h.

9. Method according to claim 8, characterised in that, the duration of the gas stripping is comprised between 1-10 h.

10. Method according to on ore more of the preceding claims, characterised in that the oil is protected from oxidation during the heat treatment by a blanket of nitrogen.

11. Refined triglyceride oil obtainable by the method according to one or more of the preceding claims.

12. Refined triglyceride oil, characterised by a free fatty acids content of at least 0.1 wt.%, a POV-value less than 1 and a bland flavour.

13. Refined triglyceride oil according to claim 12, characterised by a POV-value less than 0.5.

14. Edible composition containing a refined triglyceride oil according to claims 11-13.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/EP 93/03213

A. CLASSIFICATI N OF SUBJECT MATTER
IPC 5 C11B3/00 A23D9/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C11B A23D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DATABASE WPI Week 7646, Derwent Publications Ltd., London, GB; AN 76-85773X & JP,A,51 109 908 (ASAHI ELECTROCHEM IND KK) 30 September 1976 see abstract	1,11-14 5,6
A	---	1,11-14
Y	DATABASE WPI Week 8047, Derwent Publications Ltd., London, GB; AN 80-83759C & JP,A,54 088 904 (NISSHIN OIL MILLS KK) 14 July 1979 see abstract	2
A	---	
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AU,B,632 272 (PALM OIL RESEARCH INSTITUTE OF MALAYSIA) 14 September 1989 see the whole document	1,2,7, 11-14
A	EP,A,0 269 277 (THE CAMBRIAN ENGINEERING GROUP LIMITED) 1 June 1988 see examples 1,6	1,5,6, 11-14
A	DE,A,38 39 017 (HENKEL) 23 May 1990 see claims 1,4,6	1,7, 10-14
A	GB,A,1 510 056 (ASAHI DENKA KOGYO K.K.) 10 May 1978 see the whole document	1,11-14
A	EP,A,0 405 601 (SOCIEDAD ESPANOLA DE CARBUROS METALICOS S.A.) 2 January 1991 see claim 1	1,11-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/EP 93/03213

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